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# Studies on the Joint Reaction Concerning Acetylene

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CITATION:

Furukawa, Junji ...[et al]. Studies on the Joint Reaction Concerning Acetylene. Bulletin of the Institute for Chemical Research, Kyoto University 1953, 31(2): 139-140

ISSUE DATE:

1953-03-30

URL:

<http://hdl.handle.net/2433/75290>

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Table 2.

|   | Ba-0 | Ba-20 | Ba-40 | Ba-50 | Ba-60 | 331 | 331' |
|---|------|-------|-------|-------|-------|-----|------|
| Linear thermal expansion coefficient ( $\times 10^{-7}$ ), (20~350°C) | 86   | 86    | 87    | 89    | 97    | 82  | 81   |
| Firing temp. (°C)   | 770  | 765   | 960   | 965   | 970   | 910 | 900  |
| Softening temp. (°C)  | 545  | 595   | 670   | 690   | 665   | 710 | 700  |
| Transformation temp. (°C)   | 487  | 525   | 605   | 640   | 625   | 670 | 650  |

(2) **The influence of mill addition.** For the purpose of investigating the effect of mill addition, 10 parts of feldspar, alumina, silica *etc.* were respectively added to 100 parts of the frit No. 331' at the milling. The similar characteristic properties given in the preceeding table have been measured, whose results are summerized in Table 3. In this case, however, the samples for measuring the expansion were prepared by the rod method given by Andrews (J. Am. Cer. Soc., **16**, 338 (1933)). From the data it can be concluded that such mill addition as chromium oxide may be effective for raising the firing temperature without decreasing the expansion coefficient.

Table 3.

|  | CuO | NiO | CoO | Feldspar | Cr <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> |
|--|-----|-----|-----|----------|--------------------------------|------------------|------------------|--------------------------------|
| Linear thermal expansion coefficient ( $\times 10^7$ ), (20~350°C) | 83  | 81  | 82  | 81       | 82                             | 79               | 74               | 75                             |
| Firing temp. (°C)  | 895 | 895 | 900 | 920      | 925                            | 920              | 945              | 975                            |
| Softening temp. (°C)   | 625 | 680 | 675 | 695      | 710                            | 710              | 720              | 710                            |
| Transformation temp. (°C)  | 575 | 630 | 615 | 635      | 650                            | 665              | 650              | 650                            |

#### 14. Studies on the Joint Reaction Concerning Acetylene

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We have examined the joint reaction concerning acetylene. In the present paper, the results of the direct joint reaction and related discussions are reported.

Diethylamine and acetylene were jointed by CH<sub>2</sub>O and propargyl amine was produced. On the other hand, dimethylamine hydrochloride did not reacted under the same condition of reaction. Ammonium chloride and

acetylene were not jointed, but propargyl alcohol and butyndiol were produced by the reaction between acetylene and  $\text{CH}_2\text{O}$ . Acetoacetic ethyl ester was not jointed with acetylene, but viscous high molecular compounds were produced by multiple jointing with themselves. Carbazol was not jointed with acetylene, but methylene-bis-carbazol was produced by jointing with themselves. Diethylaniline, also, gave rise to methylene-bis-dimethylaniline. Acetone, diphenylamine, and thiourea did not react with acetylene or with  $\text{CH}_2\text{O}$ .

On the other hand, we arranged systematically the examples of the general joint reactions which had been performed up to date. Then, an important fact was pointed out; that is, one of the two passive components in the direct reaction should be limited to those compounds which consisted exclusively of amino-compounds ( $\text{R}_2\text{NH}$ ,  $\text{RNH}_2$  and  $\text{RCONH}_2$ , etc.) with the exception of  $\text{HCl}$ . From this empirical fact, it appears that acetylene can hardly be jointed with passive components other than aminocompounds.

In order to clarify the above empirical fact, we analysed the joint reaction from the standpoint of the bond energy. Recently, one of us discovered (J. Furukawa: Lecture at the symposium of the Chemical Society of Japan. Oct., 25, 1952 in Osaka.) that bond energy consists of both covalent and ionic terms, viz.,  $D_{x-y} = J_x + J_y - e_x \cdot e_y$  ( $J$  and  $e$  are the covalent and ionic terms respectively). Now, it is probable to assume that the decisive factor of the reactions is the heat of reactions. Thus, comparing the bond energy, the necessary conditions for the direct reaction was proved to be (details of calculation are omitted)

$$J_A < J_B, \quad |e_A| > |e_B|$$

Now,  $J$  and  $e$  values of some typical passive components are as follows:

|                                 | $J$   | $e$   |
|---------------------------------|-------|-------|
| $(\text{CH}_3)_2\text{N}:$      | 9     | -5    |
| $\text{CH}_3\text{NH}:$         | 10    | -5    |
| .....                           | ..... | ..... |
| .....                           | ..... | ..... |
| $\text{CH}_3\text{O}:$          | 40    | -     |
| $\text{C}_3\text{H}_7\text{O}:$ | 27    | -3    |
| $:\text{C}\equiv\text{N}$       | 63    | -2.5  |
| $:\text{C}\equiv\text{CH}$      | 63    | -     |

Comparing these values with the above conditions, the empirical fact and our experimental results are well understood in agreement with the theoretical stand point.